

(19) World Intellectual Property
Organization
International Bureau



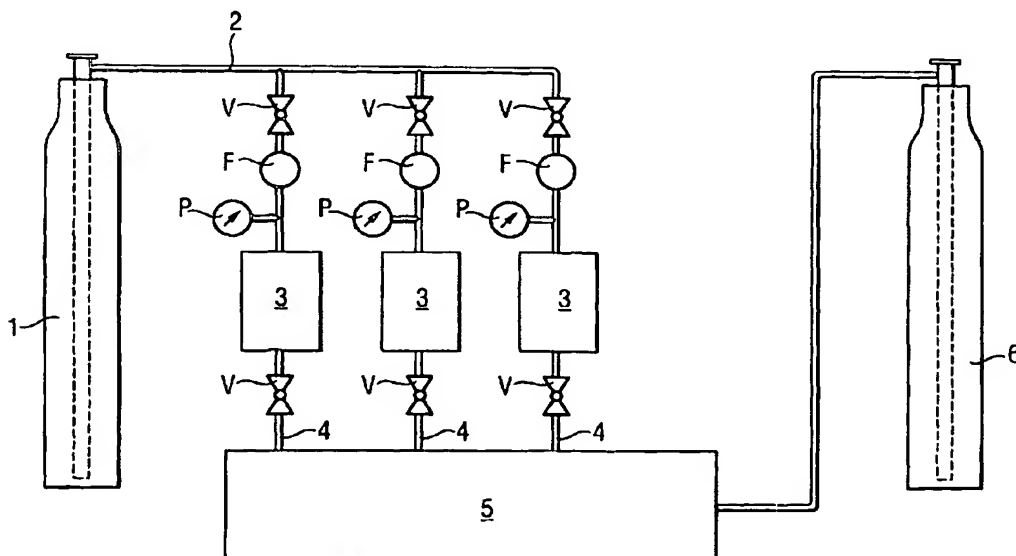
(43) International Publication Date
22 January 2004 (22.01.2004)

PCT

(10) International Publication Number
WO 2004/007368 A1

- (51) International Patent Classification⁷: **C01B 33/158**,
B01J 13/00
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- (21) International Application Number:
PCT/EP2003/006606
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 24 June 2003 (24.06.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
NO2002A000010 12 July 2002 (12.07.2002) IT
- (84) Designated States (*regional*): European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR).
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- Declaration under Rule 4.17:**
— *of inventorship (Rule 4.17(iv)) for US only*
- (72) Inventors; and
- Published:**
— *with international search report*
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- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: METHOD FOR THE PREPARATION OF AEROGELS



(57) Abstract: The present invention is concerned with a method for the preparation of aerogels that includes a phase of exchange with the liquid present in the aquagel by the liquid xenon and the subsequent extraction thereof.

Method for the preparation of aerogels

The present invention is referred to a process for the preparation of aerogels including an exchange phase of the liquid present in the wet gel by xenon and a following extraction of very xenon.

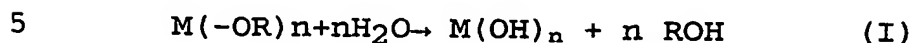
Aerogels are one of possible products of a sol-gel process. Aerogels, up to now, have found application mainly in the thermoacoustic insulation and in chemical catalysis, as well as intermediate materials in production of glasses and glass ceramics; a new application, currently under study, is an insulation layer of very low dielectric constant in the production of integrated circuits.

It is known that the sol-gel processes are chemical processes according to which a material is produced from a mixture of suitable precursors (called sol), such a material being typically a simple or mixed oxide either as a bulk or as a thin layer onto a carrier.

Sol-gel processes are the subject of important published patent documents and are described, for example, in the following patents: US-A-4.574.063, US-A-4.680.048, US-A-4.810.674, US-A-4.961.767 and US-A-5.207.814.

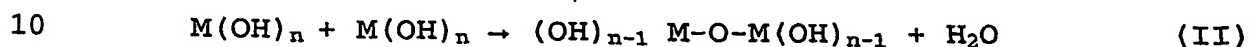
Water, alcohols and water/alcohol mixtures are usually employed as solvent/diluent for the starting solution, the precursors may be soluble salts of metals and/or of metalloids, for example nitrates, chlorides and acetates or preferably they may be compounds of the general formula $M(OR)_n$ where M is the metal or metalloid atom, O-R is an alcoholic radical (typically from an alcohol containing from one to four carbon atoms) and n is the valence of M. Among the most frequently used precursors in sol-gel processes are tetramethoxysilane (known as TMOS) with the formula $Si(OCH_3)_4$ and tetraethoxysilane (known as TEOS) with the formula $Si(OCH_2CH_3)_4$.

The first phase of a sol-gel process is the precursor hydrolysis from water that may be present as solvent or be purposely added in the case of alcoholic solutions, according to the reaction:



This phase is generally helped by low pH values: typically between 0 and 3, preferably between about 1 and 2.

The second phase in the sol-gel process is the condensation of the $M(OH)_n$ species according to the following scheme:



This reaction, extended to all the $M(OH)_n$ species originally present in solution, leads to an inorganic oxidic polymer with an open structure inglobating within its porosity all the solvent originally present or
15 generated during the hydrolysis. The inorganic, oxidic polymer so produced is called gel.

To find practical application, the gel needs to be dried by careful extraction of all liquid from its pores.

20 A possible method of drying a gel is by simple solvent evaporation; the dry gel so produced is known as a "Xerogel". As it is known to the experts in the field, the production of xerogels is extremely difficult because of the strong capillary forces produced by the solvent on the
25 pore wall: during evaporation, that normally lead to the destruction of the gel.

An alternative method for producing dry gels is the supercritical (or hypercritical) extraction of the solvent. Dry gels produced by this technique are known as
30 "Aerogels".

During the hypercritical drying in suitable autoclaves the liquid present in the gel is subjected to values of temperature and pressure that exceeds the critical values specific for that liquid. At that moment the whole liquid volume passes from the liquid phase to that of supercritical fluid and the related capillary forces inside the pores decrease from the initial value to the reduced value proper of the supercritical fluid. It is so avoided the destructive phase of the meniscus presence inside the pores that is always produced by evaporations during the preparation of xerogels. The technique of hypercritical extraction of a liquid from a gel is described, for example, in

US-A-4.432.956 e US-A-5.395.805. The main problem with this technique is that alcohols, normally present in the gel pores have critical pressure P_c typically above 60-70 bars and critical temperatures T_c above 250°C. Such critical values mandate the use of autoclaves of high resistance and relatively high cost. Moreover, if the gel product is in the form of film on support (for example in the case of a dielectric insulating film on an integrated circuit), the critical temperatures of alcohols and esters might be too high and not compatible with the support or with other materials present on it.

A well known technique to overcome the problem is through the liquid exchange in the wet gel before hypercritical extraction, with a liquid of more favorable critical constants, particularly of lower T_c . For example, it is possible to use hydrocarbons, as pentane and hexane, that have critical temperature in the range of 200°C. Even in this case, however, the T_c value might be not compatible with all the applications predictable with aerogels; moreover the exchange of an hydroalcoholic liquid with an hydrocarbon, because of the non mixibility of these liquids would require an additional exchange with intermediate

liquids as, for example, acetone, with the consequent expansion of the process time and of the cost of recycling the organic solvents.

5 Still another possibility is to exchange the hydroalcoholic liquid with liquid CO₂, that has a very favorable T_c value (about 35°C); also this liquid, however, is not miscible with water and requires the use of an intermediate exchange liquid. Acetone, in this case, is not suitable because, if mixed with liquid CO₂, prevents it from entering
10 hypercritical transition; it is possible to use, as an intermediate exchange liquid, isoamylacetate; but, also in this case, the double exchange (acetone first, amylacetate after) requires process-time excessively long for an industrial process and undesirable solvent-recycling costs.

15 The Applicant has now found that it is possible to prepare the aerogels without no drawback among the ones belonging to the known art and, according to a preferred embodiment, through a hypercritical extraction step carried out at moderate pressure and temperature values which,
20 furthermore, does not need long times in the preceding liquid exchange in the wet gel.

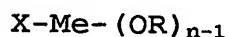
As a matter of fact, an object of the present invention is a method for the preparation of aerogels comprising the exchange of the aquagel liquid phase with xenon, the
25 extraction of xenon and the possible recover thereof; particular advantages are achievable by carrying out the exchange with liquid xenon and the extraction thereof under supercritical conditions.

The aquagel preparation can be made following one of the
30 preparative process reported in the state of the art; for example, by hydrolysis of a suitable precursor. In this case, the process will involve a preliminary step of hydrolysis/condensation starting from the suitable precursor.

A peculiar embodiment of the present invention is the preparation of the aerogels including:

- a) hydrolysis/condensation starting from a precursor;
- b) exchange of the liquid in the gel with xenon
- 5 c) supercritical extraction of xenon
- d) possible xenon recovering.

The metallic precursor undergoing the hydrolysis reaction may be whatever compound known in the art. Therefore, use may be made of soluble salts such as, for instance,
10 nitrates, chlorides and acetate; moreover, use can be made, according to the best carrying out, of alcoxydes or alcoxyde mixtures having the general formula:



wherein Me is a metal of the 3rd, 4th and 5th Groups of the
15 Element Periodic System; n is Me valence; X is R or OR, R being acid alkyl radical, linear or branched, having a carbon atom number up to 10.

The hydrolysis is carried out in the presence of a catalyst, preferably of the acid kind, and water may be the
20 solvent, or it may be added to the precursor alcoholic solution; the relevant conditions and procedure are reported in the known art such as, for instance, the one corresponding to US patent no.5.207.814 according to which the hydrolysis is carried out at room temperature and
25 preferred acid catalysts are chloride acid, nitric acid and acetic acid. Metal oxides, mainly silicon oxide, can be added to the prepared sol to modify the properties thereof, according to, for instance, US patent no.5.207.814.

The liquid present in the wet gel is exchanged with xenon
30 having critical temperature, $T_c = 16,6^\circ\text{C}$ and critical pressure, $P_c = 58,4$ bars, over very short times. Once the

exchange is completed, xenon is easily extracted without any use of autoclave suitable for high temperature and pressure.

5 Xenon, as known, is a gas at atmospheric pressure and temperature; it belongs to the class of the so called rare gases, and traditionally is utilized in discharge lamps, in solar lamps, in arc lamps for the production of U.V. radiations, to excite laser cavities, for ionization chambers, in the bubble chambers for the detection of
10 elementary particles.

For the purposes of the current invention, the xenon is maintained liquid with pressure above 58,4 bars and temperature below 16,6°C, preferably below 10°C. To favor interdiffusion processes in the liquid phase within the
15 pore structure, xenon temperature should be not as low, usually not lower than 0°C.

Considering the high cost of xenon, the method of the invention is preferably used with systems that provide the recovery of xenon at the end of the extraction process.

20 A possible scheme of this type of system is indicated in Fig.1, to which we here refer merely as an example excluding any restrictive consideration.

System A of Fig.1 is an example of process of hypercritically drying an aquagel using exclusively xenon.
25 The system includes a reservoir of liquid xenon 1, connected through a line 2 to at least one, but preferably several moulds 3, (Fig.1 shows a system of 3 moulds) containing the original aquagels. The moulds are connected with discharge lines 4, for the liquid exchanged in the
30 pores (water and/or alcohol) and gaseous xenon at the end of the supercritical extraction process. All lines 4 are converging into one suitable collector 5, with proper temperature under which water and alcohol are solid while

xenon is in the liquid phase, for example at a temperature between about -30°C and -40°C . Finally collector 5 is connected to a reservoir 6 for the recovered xenon, that in certain models could be the same reservoir 1. The system is supplied with open/closed valve, identified as V in Fig.1, that provide selective insulation of any component of the system. In addition, on the line 2 before each mould 3, there can be connected flow-meters F, to regulate xenon flux in each mould; to each mould is connected a pressure gage P, to control pressure in each mould.

More in general, liquid xenon at temperatures between 0°C and 16°C can be flown inside the aquagels to replace the liquid originally contained so that a xenongel is obtained. The xenongel is then subjected to hypercritical or supercritical drying at a temperature above $16,6^{\circ}\text{C}$ and pressure above 58,4 bars.

Claims:

1. A process for the preparation of aerogels including:

-the exchange of the liquid phase of the aquagel with xenon;

5 -the extraction of xenon and the possible recovery thereof.

2. A process for the preparation of aerogels according to claim 1, including a previous phase of hydrolysis/condensation of the suitable precursor.

10 3. A process for the preparation of aerogels according to claim 2, where the hydrolysis/condensation reaction is carried out starting from an alkoxyde precursor of the formula:



15 in which Me is a metal belonging to the 3rd, 4th and 5th Groups of the Element Periodic System; n is integer and represents the valence of Me; X is either -OR or -R where -OR is an alkoxyde group and -R is an organic radical linear or branched with a number of carbon atoms
20 up to 10.

4. A process for the preparation of aerogels according to claim 3 where the suitable precursor is preferably tetramethoxysilane, tetraethoxysilane.

25 5. A process for the preparation of aerogels according to claim 3 where the hydrolysis reaction is accomplished in presence of an acid selected among hydrochloric, nitric or acetic acid.

30 6. A process for the preparation of aerogels including the exchange of the aquagel liquid phase with xenon according to claim 1 where such an exchange is

accomplished with liquid xenon and the extraction thereof is accomplished under supercritical conditions.

- 5 7. A process for the preparation of aerogels according to claim 6 where the exchange of the liquid in the aquagel is carried with liquified xenon at temperature between 0 and 16.6 °C.
- 10 8. A process for the preparation of aerogels according to claim 6 where the hypercritical extraction of xenon from the wet gel is carried a temperature higher than 16.6 °C.
9. A process for the preparation of aerogels according to claim 6 where the hypercritical extraction of xenon is carried at a pressure higher than 58.4 bar.
- 15 10. A process for the preparation of aerogels including the exchange of the aquagel liquid phase with xenon according to claims 1 and 6 characterized in that it comprises also a xenon recovering phase at the end of the extraction.